The sorption of Volatile Organic Compounds (VOCS) by modified MDF panels and effects on mould colonisation and growth

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THE SORPTION OF VOLATILE ORGANIC COMPOUNDS (VOCS) BY MODIFIED MDF PANELS AND THE EFFECTS ON MOULD COLONISATION AND GROWTH

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ABSTRACT

The increased effort to improve energy efficiency, has led to improved "air-tightness" of buildings, therefore leading to a reduction in ventilation. This results in an increase in concentration of indoor air pollutants, such as formaldehyde and volatile organic compounds (VOCs). VOCs are suspected to contribute to "sick building syndrome" (SBS), causing headaches and depression and can act as an irritant to skin, eyes and the respiratory system. The sources of VOCs are vast, ranging from humans, carpets, sealants, burning organic material, wood and cleaning products. Over the years, there has been considerable research into the reduction of emissions from their original source and modifying current construction products to actively absorb air pollutants, when in service. Such modifications include use of bio-resins, odourless paints and inorganic and organic additives to products.

One modification is to use solid additives, termed "scavengers" in wood-based panels. However, the use of such organic additives may cause an increase or decrease of a panel's vulnerability to biological activity. This paper examines the effects of these scavengers on mould growth and the absorption of the VOCs: toluene, limonene and formaldehyde. Additionally, the effect of the sorption of VOCs on the colonisation and growth of different mould species on modified MDF panels, was also studied.

INTRODUCTION

In recent years, indoor air quality and volatile organic compounds (VOCs) have received increasing attention. Coupled with this, there is an increased effort to improve the energy efficiency of buildings, which has resulted in the improved "air tightness" of buildings. An adverse effect of this, however, is the increase in the concentration of air pollutants, such as VOCs, inside homes where concentrations of many pollutants can be higher than in the outdoor environment (Rong *et al.,* 2002). These VOCs often cause sick building syndrome (SBS) and have a number of symptoms: dizziness, eye and lung irritation, nausea and depression (Zhang and Xu, 2003). Therefore, indoor air quality has become an issue of public health (Kim *et al.,* 2011).

The World Health Organisation defines VOCs as compounds with a boiling point between 50^{o}C to 260^{o}C (WHO, 1989), which encompasses a great variety of compounds including, hydrocarbons, terpenes and aromatic hydrocarbons. Indoor air pollutants can be further classified into three groups: Very volatile (gaseous) compounds (VVOC) with boiling point of >0 – 50°C, Volatile organic compounds (VOC) with boiling points of 50 – 100°C to 250 – 260°C and semi-volatile organic compounds with boiling point of 240 – 260°C to 380 – 400°C (Roffael *et al.,* 2015). Therefore it is an immense challenge to develop a product that will act as a sink to all VOCs.

Historically, there has been considerable research into the reduction of emissions from their original source, such as odourless paints and replacing formaldehyde based resins with bio-based resins during wood-based panel production. More recently, there have been investigations into modifying wood-based construction materials and insulation materials to actively absorb formaldehyde and VOCs from the atmosphere.

One such modification is to use chemical and solid additives, termed "scavengers", in wood-based panels, to bond with free VOCs and formaldehyde. These scavengers are added to panels during production, directly as part of the resin or as a solid additive. These scavengers usually take the form of commercially available chemicals. However, recent research has shown by-products from various industries, such as waste materials (both inorganic and organic).have promise as low cost scavengers of VOCs

The use of these additives, especially organic scavengers, raises the question as to what implication this sequestering of VOCs has on the resistance of modified MDF panels to microbial growth. Moulds will attack lignocellulosic materials, seeds, seedlings, food stuffs and books (Pasanen *et al.*, 1992). Moulds can also attack synthetic floor coverings, airplane fuels, oils, glues, paints and textiles (Schmidt, 2006). Moulds rapidly colonise and grow on surface substrates and conidia develop rapidly. On timber, hyphae of mould fungi are able to penetrate the wood to a depth of a few millimetres and live on parenchyma cells that store sugar, starch and protein (Schmidt, 2006). Most moulds do not attack lignified cell walls, so therefore the wood strength properties remain unchanged (Viitanen, 1994).

However, the presence of moulds in damp buildings, can also contribute to SBS as many mould species' spores are known to cause health problems such as asthma, allergies and bronchitis (Nielsen, 2003 and Jarvis and Miller, 2005). The presence of moulds in construction materials can also increase a materials susceptibility to more destructive biological activity, such as decay fungi. Therefore it is highly important to study the implications of modifying current products to sequester VOCs on mould growth. It is widely known that the presence of formaldehyde will significantly prevent the growth of fungi on wood-based panels. However, little is known of the effects of absorbed VOCs on the colonisation and growth of moulds.

The work describes below, is an initial study developing a method to evaluate mould growth on modified MDF boards. , modified with different organic scavengers from organic waste: peanut shell and walnut shell. The sorption of water and VOCs by the modified panels was also evaluated. The modified boards were "flooded" with VOCs, formaldehyde, toluene and limonene and then exposed to five different mould species: *Trichoderma virens, Cladosporium sphaerospermum, Chaetomium globosum, Aspergillus niger* and *Penicillium rubens.*

MATERIALS AND METHOD

Materials

The chemical solutions used to represent different chemical groups of VOCs were formaldehyde, limonene and toluene. A water sorption test was also used as a control.
The materials tested were modified MDF construction materials and solid pine wood (*Pinus sylvestris*) as a control. The construction materials were modified with different VOC scavengers, walnut shells and peanut shells at three different loading percentages: 5, 10 and 15% (on a dry weight basis). The peanut shell and walnut shell were milled to a particle size of 50mm. A Control MDF without scavengers was also produced. The boards were produced using a formaldehyde based resin, therefore time was given to allow for de-gassing of free formaldehyde.
Six replicates of each material were used for the sorption test of each VOC. As the analysis of mould growth was visual, dimensions of the test specimens were not critical but were

approximately 50 x 25 mm and the thickness should be that of the test material. A further six replicates were used as sorption control specimens. All the test specimens were conditioned in standard conditions of 23ºC ±1 and 60 ±3 % RH.

Moulds

All the mould species were purchased from Fungal Biodiversity Centre, Institute of the Royal Netherlands Academy of Arts and Science (KNAW). The mould species selected for use in testing are representative of species commonly found within buildings:

1. *Cladosporium sphaerospermum* (Penz) CBS 122.63
2. *Chaetomium globosum* (Kunze ex Fr.) CBS 107.14
3. *Penicillium rubens* (Biourge) CBS 401.92
4. *Trichoderma virens* (J.H. Mill, Giddens & A.A. Foster) CBS 100946
5. *Aspergillus niger* (M. Frank) CBS 101698

Preparation of spores

The fungal spore suspension was produced following BS EN 846, using well sporulated cultures of each moulds tested. 5ml of sterilised water were added to the culture and a sterile needle was used to gently scrape the spores from the surface into the water. The spore suspension was decanted off into a sterile tube and agitated using an orbital shaker and then filtered to remove mycelial fragments. The spore suspensions were combined together and agitated again.

VOC and water exposure

The VOCs chosen for this work were formaldehyde, representative of polar compounds,; toluene, representing aromatic compounds (and is similar to benzene ring); and limonene, representing non-polar compounds.

To expose the modified boards to VOCs and water, 600ml volume vessels were used. Prior to exposing the samples to the VOCs, the jars and samples were sterilised. This was achieved by spraying the inside of the jars, metal stand and the samples with 70% ethanol and allowed to dry in sterile conditions. The samples were placed on top of metal meshes, to ensure that the samples were out of contact with the solvents. Each chamber was sealed with an aluminium lid and wrapped with parafilm to ensure that no solvent was lost through evaporation. The chambers were then stored for seven days at a constant temperature and humidity of 20°C ±2 at 70% RH ±3.

Inoculation and exposure

To evaluate the "flooded" VOC samples' resistance to mould growth, the test was carried out using 600ml vessels with ventilated aluminium lids. 80ml of water agar was poured into each vessel and then autoclaved at 121°C for 50 minutes. Sterile, inert plastic meshes were added to ensure the samples were not in direct contact with the water agar.

Under sterile conditions, two of the board samples were removed from the VOC chambers and into 600ml vessels on top of the plastic mesh. Each sample was then inoculated with 0.5ml of the spore suspension. The vessels were then quickly sealed with an aluminium lid. These vessels were then stored in a dark chamber at 20°C ±2 at 70% RH ±3 for two weeks.

Assessment

For the assessment, the presence or absence of the different mould species was identified and given a score of 1 or 0. A mean value was then calculated to indicate the presence and

frequency of mould growth across all replicates. Where possible, the primary, secondary and tertiary colonisers were identified and the dominant mould species identified and recorded.

RESULTS AND DISCUSSION

VOC Sorption

Table 1, shows the results of the sorption of the four VOCs by the different modified panels. The boards containing 15% walnut absorbed the most moisture in the water chamber 1.87 g/kg and 5% walnut, the least, and 1.28 g/kg. Of the formaldehyde VOC, the blank MDF samples, absorbed the most and solid pine wood the least, 1.56 g/kg and 0.98 g/kg, respectively. Panels containing 10% peanut shall have absorbed the most limonene and solid pine the least, 1.17 g/kg and 0.35 g/kg respectively. Figure 3 graphically shows the results of the toluene sorption by the modified panels. As is obvious, the standard error bars are quite large. This is due to toluene being a volatile compound. Once removed from the chamber, the boards will de-gas and the free toluene immediately begins to evaporate.

Table 1: Shows the average sorption of VOCs by modified panels

Sample	Water (g/kg)	Formaldehyde (g/kg)	Toluene (g/kg)	Limonene (g/kg)
5 % Walnut	1.28	1.12	0.94	0.49
10 % Walnut	1.53	1.17	0.87	0.74
15 % Walnut	1.87	1.35	0.66	0.59
5 % Peanut	1.47	1.18	1.20	0.78
10 % Peanut	1.37	1.37	1.29	1.17
15 % Peanut	1.52	1.52	0.67	0.48
MDF Blank	1.56	1.56	1.00	0.91
Pine	1.43	0.98	1.55	0.35

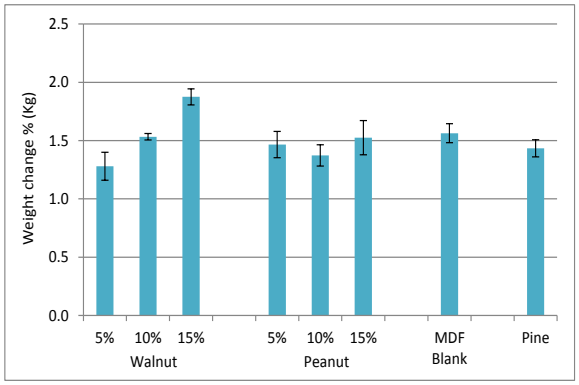

Figure 1: Water sorption

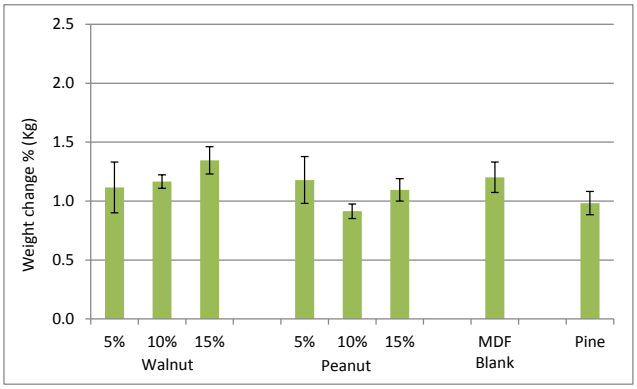

Figure 2: Formaldehyde sorption

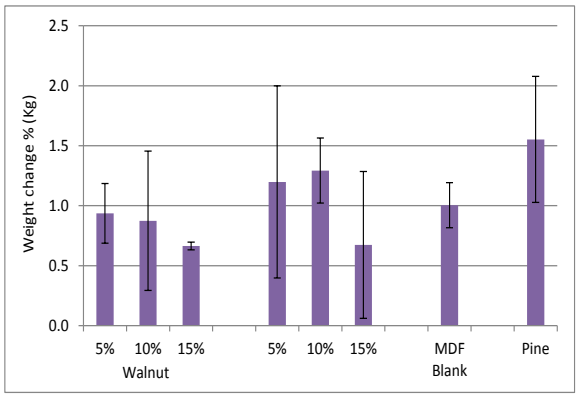

Figure 3: Toluene sorption

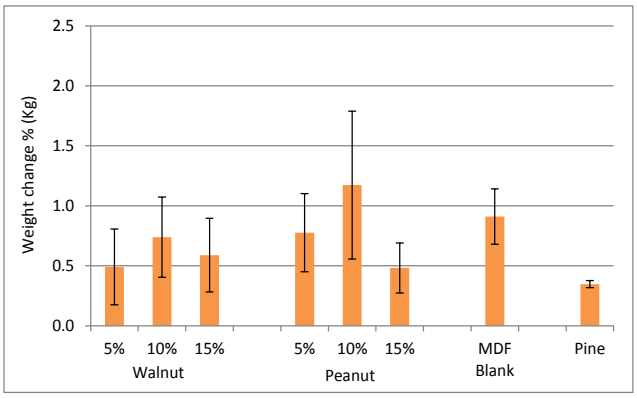

Figure 4: Limonene sorption

Mould growth

The greatest mould growth was, as expected, observed on the modified boards exposed to water. Unfortunately, *Chaetomium globosum* failed to grow across all the samples.

Water sorption

Table 2 shows the results for the mean frequency of growth of each mould species across the replicates. *Aspergillus niger* had successfully developed on all types of modified boards and was observed in all replicates. *Cladosporium sphaerospermum* and *Trichoderma virens* were also seen on all types of modified panels, but not of the same frequency as *Aspergillus niger*. *Penicillium rubens* was largely observed on all types of boards but showed the least frequency of growth. However, as a primary coloniser it may have been out-competed by the other secondary and tertiary colonisers over the two weeks.

The greatest extent of growth was observed on the 10 and 15% walnut boards. This is likely to be a result of the higher moisture content of the boards, due to absorbing more moisture when in the chamber (Figure 1).

Solid pine showed the lowest presence of mould growth across replicates. This is likely to be result of the lower moisture sorption, inhibiting the mould growth.

Table 2: Presence of mould species on samples exposed to water

Sample	*C. globosum*	*T. virens*	*C. sphaerospermum*	*A. niger*	*P. rubens*	Total frequency of growth
5 % Walnut	0	0.83	1	1	0.83	3.67
10 % Walnut	0	1	1	1	1	4
15 % Walnut	0	1	1	1	1	4
5 % Peanut	0	0.83	1	1	0.50	3.33
10 % Peanut	0	1	1	1	0	3
15 % Peanut	0	1	1	1	0.67	3.67
MDF Blank	0	0.83	1	1	0.50	3.33
Pine	0	0	0.50	1	0	1.50

Figure 5 shows the frequency of mould species growing on the different types of boards. It suggests that the addition of organic waste increases the susceptibility of the product to mould colonisation and growth.

Formaldehyde sorption

Across all the modified boards and replicates, no mould growth of any mould species was observed. Formaldehyde has been shown to be toxic to microorganisms (Rong *et al.*, 2002). Of the VOCs tested, formaldehyde was absorbed to the greatest extent by the modified boards, see Table 1. As all the boards produced underwent the same de-gassing period, mould growth was observed on water exposed samples and not observed on the samples exposed to formaldehyde, the sorption of additional formaldehyde was sufficient to prevent the establishment and growth of all mould species.

As mould growth was not observed on solid pine, this indicates that wood can absorb enough formaldehyde to prevent mould growth. However, this experiment was not continued after two weeks. Therefore it is possible that the formaldehyde was not trapped within the pine wood and would eventually de-gas and mould would colonise and grow on the wood.

Toluene sorption

Little growth was observed on the toluene exposed samples. It is possible that due to the off-gassing from the sample of free toluene, toluene gas could have accumulated inside the vessels. This accumulation of the gas could have vastly reduced the oxygen levels, therefore preventing mould growth. Over the two weeks that the test was ongoing, the oxygen levels will have increased inside the vessels, as toluene gas dispersed. As the test was left for two weeks, toluene gas will have eventually allowed primary colonisers, *Aspergillus niger* and *Penicillium rubens* to grow and establish (WHO, 2009). If allowed more time to grow, it is possible that more growth and further colonisation may occur.

Table 3: Presence of mould species on samples exposed to toluene

Sample	C. globosum	*T. virens*	*C. sphaerospermum*	*A. niger*	*P. rubens*	Total frequency of growth
5 % Walnut	0	0	0	0	0	0
10 % Walnut	0	0	0	0	0.33	0.33
15 % Walnut	0	0	0	0	0.17	0.17
5 % Peanut	0	0	0	0	0	0
10 % Peanut	0	0	0	0.33	0.33	0.67
15 % Peanut	0	0.17	0	0.33	0.33	0.83
MDF Blank	0	0	0	0	0.17	0.17
Pine	0	0	0.17	0	0	0.17

Limonene sorption

From Figure 4, it is evident that all the boards absorbed limonene whilst in the chambers. Table 4 shows the subsequent results of the mould growth on the boards. Minimal growth was observed on the 5% and 10% walnut boards and only of the primary coloniser *Penicillium rubens.* No growth was observed on all other boards. Again, it should be noted that possible de-gassing of the VOCs may have also prevented the growth of the moulds.

Table 4: Presence of mould species on samples exposed to limonene

Sample	C. globosum	*T. virens*	*C. sphaerospermum*	*A. niger*	*P. rubens*	Total frequency of growth
5 % Walnut	0	0	0	0	0.67	0.67
10 % Walnut	0	0	0	0	0.33	0.33
15 % Walnut	0	0	0	0	0	0
5 % Peanut	0	0	0	0	0	0
10 % Peanut	0	0	0	0	0	0
15 % Peanut	0	0	0	0	0	0
MDF Blank	0	0	0	0	0	0
Pine	0	0	0	0	0	0

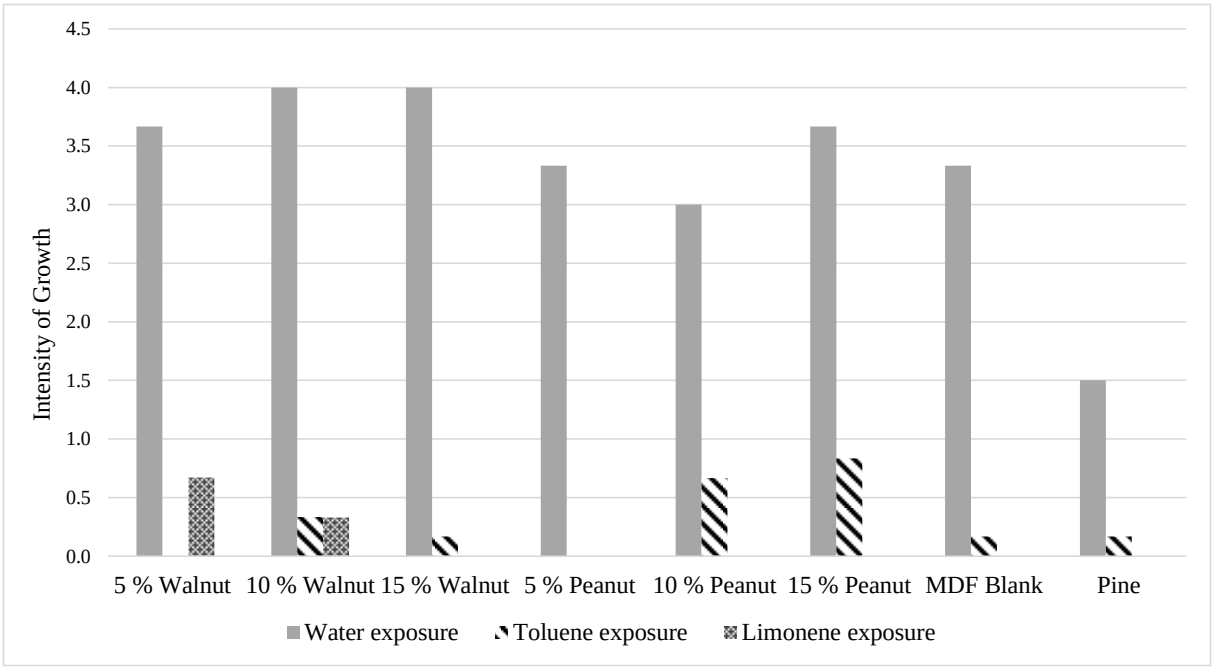

Figure 5: Presence of mould species on modifed boards after VOC and water exposure

Dominating species

Table 5 shows the dominant species found on the different types of modified boards for water, toluene and limonene. The mould growth observed on limonene and toluene exposed samples, is by the primary coloniser *Penicillium rubens.* Primary coloniser *Aspergillus niger*, was observed only on boards containing 15% peanut exposed to toluene.

Table 5: Dominant species found on modified boards

Sample	Water	*Toluene*	*Limonene*
5 % Walnut	*Aspergillus niger*	-	*Penicillium rubens*
10 % Walnut	*Cladosporium sphaerospermum,*	*Penicillium rubens*	*Penicillium rubens*
15 % Walnut	*Cladosporium sphaerospermum, Aspergillus niger*	*Penicillium rubens*	-
5 % Peanut	*Cladosporium sphaerospermum, Aspergillus niger*	-	-
10 % Peanut	*Trichoderma virens, Aspergillus niger*	*Penicillium rubens*	-
15 % Peanut	*Aspergillus niger,*	*Penicillium rubens, Aspergillus niger*	-
MDF Blank	*Aspergillus niger, Cladosporium sphaerospermum*	-	-
Pine	*Aspergillus niger*	-	-

Key: - no mould growth observed

On board samples exposed to water, a different succession of growth was observed. On boards containing 5% walnut, although Table 2 shows primary, secondary and tertiary species present, the dominant mould species was a primary coloniser. *Aspergillus niger* was also a dominant species on the boards containing 15% walnut. This suggests a slower succession of growth of the mould species grown on boards containing a walnut scavenger.

There was a lower frequency of growth of mould species on the boards containing peanut shells, when compared against those boards containing walnut shell. There was also a difference in the specific species growing and their prevalence on the peanut samples. Although primary colonisers are still present, the secondary and tertiary colonisers are more dominant. This suggests a difference in the growth rate of the moulds on boards containing peanut shell, compared to boards containing walnut shell.

CONCLUSION

The aim of this paper was to evaluate the addition of organic scavengers, absorbing VOCs and the effect this has on mould growth. The study conducted suggests that the addition of the walnut shell increases the boards' susceptibility to mould colonisation and growth. This is possibly due to an increased moisture uptake by the walnut. The presence of peanut scavenger also seems to increase vulnerability but to a lesser extent. It can also be concluded that the boards modified by the addition of walnut shell or peanut shell do absorb formaldehyde, toluene and limonene. The absorption of formaldehyde from the atmosphere by the scavengers prevents all mould growth. This sorption of VOCs does effect mould growth on

boards, reducing frequency of mould species growing, as well as causing a variation in the presence of different mould species.

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REFERENCES

EN ISO 846: 1997, Plastics – Evaluation of the action of microorganisms, Second edition 1997

JARVIS B.B and MILLER J.D (2005) Mycotoxins as Harmful Indoor Air Contaminants. Microbial Biotechnol 66: 367-372

KIM D, PARK J.H, KIM S, LEE J, YIM J, JEON J, PARK S and PARK Y (2011) Comparison of removal ability of indoor formaldehyde over different materials functionalised with various amine groups. Journal of Industrial and Engineering Chemistry. 508: 5-9

NIELSEN K.F. (2003) Mycotoxin Production By indoor Moulds. Fungal Genetics and Biology 39: 103-117

PASANEN A.L, JUUTINEN T, JANTUNEN M.J and KALLIOSKI P (1992) Occurrence and Moisture Requirements of Microbial Growth in Building Materials. International Biodeterioration and Biodegradation 30: 273-283

ROFFAEL E, SCHNEIDER T and Dix B (2015) Effect of oxidising and reducing agents on the release of volatile organic compounds (VOCs) from strands made Scots pine (*Pinus sylvestris* L.). Wood Sci Technol, 49:957 - 967

RONG H, RYU Z, ZHENG J and ZHANG Y (2002) Effect of air oxidation of Rayon-based activated carbon fibres on the absorption behaviour for formaldehyde. Carbon 40: 2291-2300

SCHMIDT O (2006) Wood and Tree Fungi; Biology, Damage, Protection and Use. Springer-Verlag Berlin Heidelberg

VIITANEN V (1994) Factors affecting the development of biodeterioration in wooden constructions. Materials and Structures, 27: 483 – 493

WORLD HEALTH ORGANIZATION (1989) Indoor Air Quality: Organic Pollutants. EURO Reports and Studies No. 111, World Health Organization, Copenhagen

WORLD HEALTH ORGANIZATION (WHO) (2009) WHO Guidelines for indoor air quality: dampness and mould. World Health Organisation, Druckpartner Moser, Germany.

ZHANG Y and XU Y (2003) Characteristics and correlations of VOC emissions from building materials. International Journal of Heat and Mass Transfer 46: 4877-4883